Amine-Functionalized Self-Pillared Pentasil (SPP) MFI as a Novel Acid-Base Bifunctional Catalyst

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Abstract

Self-pillared pentasil (SPP) MFI is a novel hierarchical zeolite material with a simple and economic synthetic route that has potential use in designs for acid-base bifunctional catalysts. With a high abundance of Brønsted acid sites, aluminosilicate SPP MFI have unique advantages in catalyzing hydrolysis of acetal compounds, which can form aldehydes that can proceed to participate in the Knoevenagel condensation. Immobilization of amine groups through grafting has been shown to produce a catalyst that can catalyze a cascade of acetal hydrolysis and Knoevenagel condensation to near completion within 10 hours. Additionally, the incorporation of palladium nanoparticles can create a catalyst with a further function of selectively hydrogenating the carbon-carbon double bond of the Knoevenagel product, which will require assessment in terms of its performance and reusability in further kinetic experiments.

Introduction

Nanostructured porous materials in general act as good supports for heterogeneous catalysis. They are particularly useful for immobilizing incompatible catalytic groups, that would otherwise quench each other in a homogeneous system. One class of reactions that would be facilitated by supported heterogeneous catalysts would be reactions that require acid and base catalytic environments in sequential steps.[2,3] Silica-based materials possess natural acid sites in the form of silanol groups, and those with trivalent heteroatoms such as aluminum can possess Brønsted acid sites.[4-7] Basic functional groups such as amines can be immobilized on the silica surface, often through grafting of aminosilanes to retain acid and base functionalities without such groups quenching each other, and the resultant material can catalyze multistep reactions that require acid and base catalysis in a one-pot setup.[5-7] Examples of reactions or reaction sequences that are catalyzed by such acid-base bifunctional catalysts include aldol condensation, Henry condensation, and cascades such as one-pot deacetylation-Knoevenagel condensation.[5-7]

Silica-based materials can be synthesized with the more economical hydrothermal synthetic technique and are thus highly valuable subjects of study. Mesoporous silica materials, with their large surface areas, are conducive to high levels of reactivity in these reactions.[8] Zeolites typically possess stronger acid sites,[9] and a mesoporous form of zeolites could support the additional of basic functional groups. Stronger acid sites have been found less conducive to the aldol and Henry condensation reactions,[8] but will be more advantageous for a cascade reaction, since the catalysis of the acid step would be more quickly resolved. One-pot deacetylation-Knoevenagel condensation is a particular sequence of reactions appropriate for such catalysts.

Mesoporous zeolite synthesis can be achieved by pillaring, or stacking layers of 2D zeolite using a pillaring agent.[10] Its surface area of 353 m^2/g when ion exchanged for protons can be less than half of that of mesoporous silica materials. Besides this shortcoming in terms of surface area, which other mesoporous zeolites would mostly likely have, the costly and difficult synthesis of 2D zeolite sheets, and similarly costly pillaring make this technique of achieving mesoporosity in zeolites less viable. One notable alternative is self-pillared pentasil (SPP) MFI,[9] with a higher surface area and higher conduciveness to internal diffusion due to its single-cell thickness, than the organic pillared MFI and a

simple one-pot synthesis technique. The pillaring in SPP MFI is also crystalline, which means the mesoporous structure is more stable in solutions of higher temperatures, and can be retained after calcination, allowing for a higher degree of flexibility in treatment and use. The use of SPP MFI functionalized with amine through aminosilane grafting for Knoevenagel condensation can be studied to investigate the properties of SPP MFI for catalyst support.

Knoevenagel condensation products have both carbon-carbon and carbonyl double bonds, and selective addition of the carbon-carbon double bond may give valuable products, and the performance of the catalyst with the incorporation of transition metal nanoparticles that give selectivity towards the carbon-carbon double bond will be an area of interest for further study. A one-pot, three-step cascade reaction of deacetylation, Knoevenagel condensation, and addition can help investigate the material's potency in acid-base bifunctional catalysis as well as the ability to incorporate metal nanoparticles for selective hydrogenation. The small unit cell size and consistent mesopores throughout the structure should help with the rate of hydrogenation with an increased surface area of metal nanoparticles after incorporation, which kinetic experiments will be designed to verify. Palladium nanoparticle incorporation in other support mediums have shown the ability to selectively catalyze the addition, and an SPP MFI can be modified to accomplish the same goal.[11]

The objective of the study is to investigate whether the structural properties of large surface area, small unit cell, and mesopores found in SPP MFI are advantageous for acid-base bifunctional catalysis. With the presence of mesopores in SPP MFI, shape or size selectivity is unlikely to be significant, but such selectivity can be introduced by additions of metal nanoparticles that can catalyze selective hydrogenation reaction of the Knoevenagel product. Whether it is advantageous to incorporate Pd nanoparticles into amine-functionalized SPP MFI for a one-pot three step reaction rather than using unsupported Pd for a separate reaction step can be tested. If supporting Pd nanoparticles proves advantageous through kinetic experiments, SPP MFI would prove to be a potent support material for various multistep reactions requiring some combination of acid, base, and transition metal catalytic environment.

Methods and Materials

SPP MFI was initially synthesized largely according to the procedure outlined in Zhang et al.[9] 0.157g of aluminum isopropoxide (Sigma Aldrich) was added to 16g of tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich) and the mixture was stirred until homogeneous. 15.923g of aqueous solution of tetra(n-butyl) phosphonium hydroxide (TBPOH, 40 wt%, Sigma Aldrich) was then added to the mixture. 0.254g of sodium hydroxide was added and the mixture was stirred until homogeneous, which is then followed by 7.028g of deionized water. The gel was stirred overnight and heated in an autoclave at 120°C for 5 days. Later syntheses are carried out with a similar recipe but adjusted duration and temperature to 115°C for 7 days, according to Xu et al., to ensure consistency in crystallization and pillared morphology. The resulting material was calcined and then ion exchanged by stirring the material in 20 weight equivalents of 1M ammonium nitrate aqueous solution at 80°C for 5 hours and filtering the slurry to collect the solid. The ion exchange was carried out 4 times and the material was calcined again to obtain the proton form of the material. 3-aminopropylriethoxysilane is added to the material and stirred with the addition of toluene as a solvent to add basic functionality. The resulting mixture was filtered and washed with a 1:1:1 by volume mixture of toluene, hexane, and ethanol. To incorporate palladium nanoparticles, a solution of H_2PdCl_4 was diluted with water and added to the grafted SPP MFI to achieve a set wt% of palladium, reduced with the addition of $NaBH_4$ and then filtered and washed with deionized water.

X-ray diffraction pattern was measured using a PANalytical X'pert Pro diffractometer operating at 40 kV and 40 mA. N_2 physisorption isotherm was measured using a Micromeritics ASAP 2020 analyzer at 77 K. SEM images were obtained on a Hitachi SU8010 microscope operating at 1 kV. Amine loading was verified through measurement of nitrogen content by sending samples of the grafted SPP MFI to Atlanta Microlabs for Elemental Analysis (EA).

The one-pot two-step cascade reaction mixture is that from Ge et al, as shown .[9] scaled to half its contents. 6 mL ethyl cyanoacetate (Sigma Aldrich) and 30 mg catalyst were mixed with 2 mmol of dimethoxybenzene (TCI) as the internal standard and 2 mmol deionized water, before being heated to 90°C with stirring, at which 2 mmol benzaldehyde dimethyl acetal (Alfa Aesar) is added to the reaction mixture. Before the reaction setup, the catalyst was heated at 80°C under high vacuum to desorb potential moisture and organics. The three-step cascade will require an additional hydrogen feed at 1 atm as reactant with the other conditions remaining constant. Reaction mixtures at selected time points of the reaction were taken to be analyzed with a GC-FID and will be compared to a calibration curve to obtain precise concentration values and conversion.

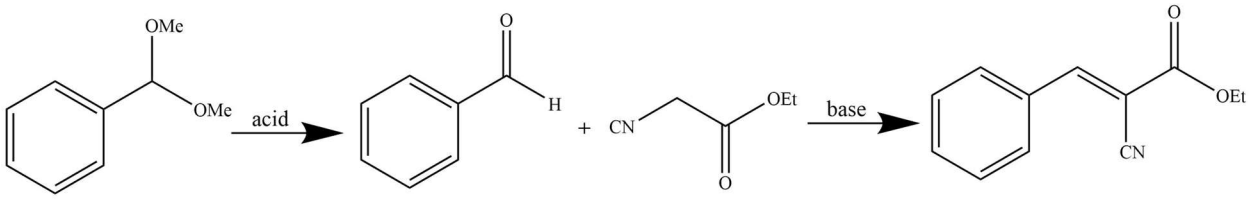

Figure 1 – Acetal Hydrolysis – Knoevenagel Condensation Cascade

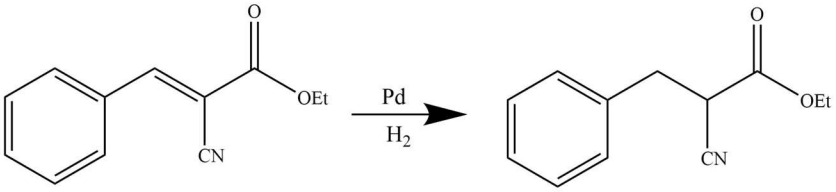

Figure 2 – Selective Hydrogenation of the Knoevenagel Product

Preliminary Results

The major wide-angle peaks of the XRD pattern (Fig. 3a) obtained for aluminosilicate SPP MFI are clustered at 7-10 degrees and at 22-25 degrees, consistent with that of conventional MFI (Fig. 3b), with differences only in intensity ratios.

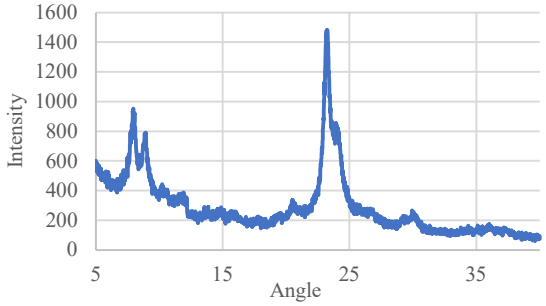

Figure 3a – Si/Al = 75 SPP MFI XRD pattern

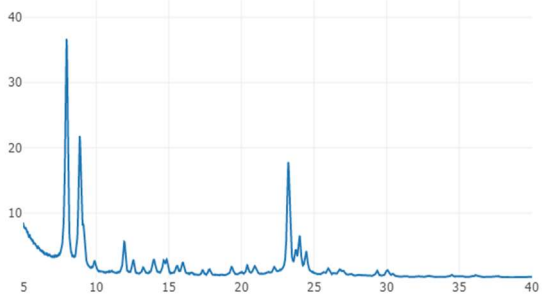

Figure 3b – Conventional MFI XRD pattern[12]

Surface area characterizations were performed through nitrogen physisorption analysis for the bare crystalline material, as shown in adsorption isotherms (Fig. 4). The BET surface are is determined to be 517.6 m^2/g, of which 215.3 m^2/g is microporous and 302.3 m^2/g is mesoporous. The available surface area for the grafted catalyst is expected to be smaller than the bare catalyst, and will be verified in future measurements.

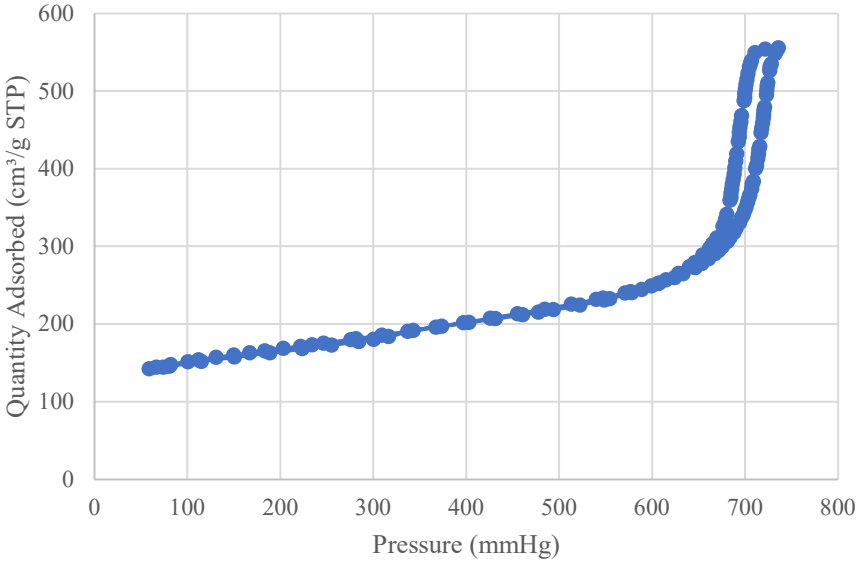

Figure 4 – Adsorption Isotherm of H^+ Form SPP MFI (Si/Al = 75)

The SEM image obtained (Fig. 5) for the material shows porous and crystalline particles that bear resemblance to the original report of SPP MFI by Zhang et al.[9]. To demonstrate the characteristic morphology cross-linking layers that form into a house-of-cards arrangement, high resolution TEM images will need to be taken. Additionally, elemental analyses demonstrated amine loadings that have little to no difference to the expected amine loading.

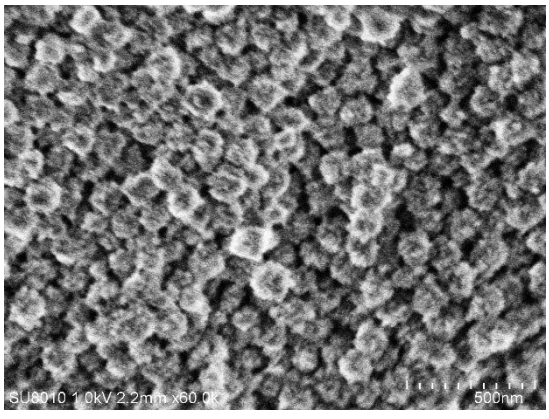

Figure 5 – SEM image of SPP MFI

Initial kinetic data of one-pot two-step cascade shows approximately 93% yield of the final product ethyl trans-α-cyanocinnamate at 10 hours. At the start of the reaction, neither step is particularly limiting, but towards the end the acid step is increasingly limiting. The relative concentrations shown in

Figure 6 are obtained through material balance and linear regression, but will be more rigorously calculated by using a calibration curve, through which absolute concentrations can also be obtained. With absolute concentration data, pseudo-first-order fitting can be done to calculate the rate constants associated with the reaction when catalyzed with amine-functionalized SPP MFI.

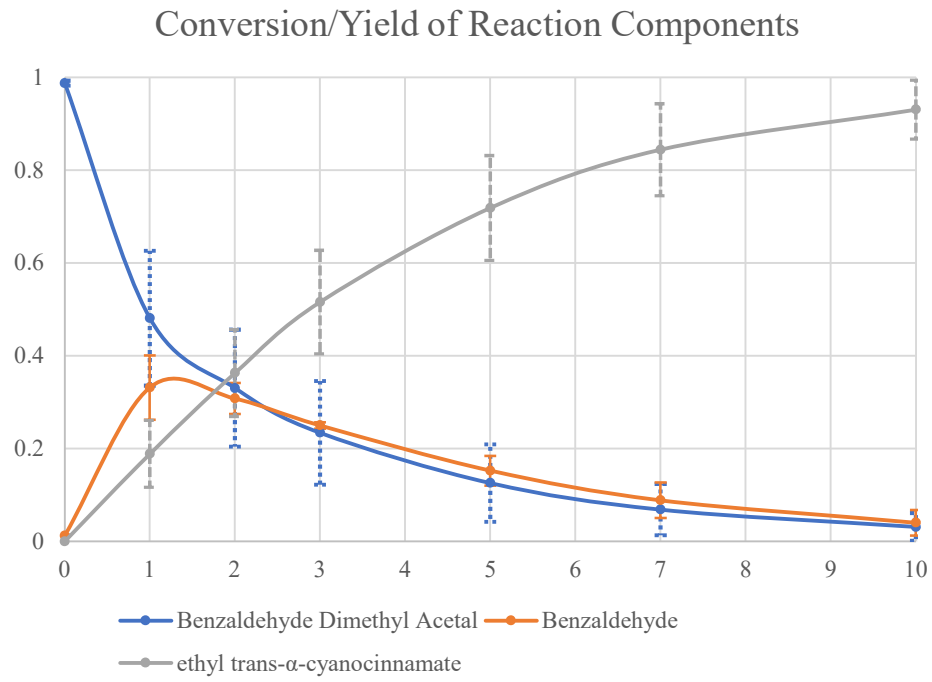

Figure 6 – Conversion/Yield of Reaction Components (95% Confidence)

Conclusions and Future Work

SPP MFI, even with inconsistent synthesis, displays a high level of acid step activity and, at appropriate nitrogen loading, gives good base step activity as well in a one-pot cascade of acetal hydrolysis and Knoevenagel condensation, nearing completion of the reaction at 10 hours. Calibration curves and pseudo-first-order fitting can be done to analyze kinetic data more completely.

In future work, the potency of the catalyst can be more fully assessed with a verified mesoporous SPP MFI ion exchanged and amine functionalized. One-pot three-step cascades with an additional hydrogenation step will be conducted with Pd-nanoparticle-incorporated SPP MFI. With adjusted amine and Pd nanoparticle loadings, the optimal catalyst for the cascade can be found. Additional studies such as pseudo-first-order fitting and recycle tests may be conducted.

References

1. A. T. Bell. The Impact of Nanoscience on Heterogeneous Catalysis. *Science* **2003**, *299*, 1688 – 1691.
2. Vera C. R.; Pieck, C. L.; K. Shimizu, Yori J. C.; Parera J. M. Pt/SO_4^{2-}-ZrO_2 catalysts prepared from Pt organometallic compounds. *Appl. Catal. A-Gen.*, **2002**, *232*, 169–180.

3. Tanabe K.; Holderich W. F. Industrial application of solid acid-base catalysts. *Appl. Catal. A-Gen.*, **1999**, *181*, 399–434.
4. Moschetta, Eric G.; Brunelli, Nicholas A.; Jones, C. W. Reaction-Dependent Heteroatom Modification of Acid-Base Catalytic Cooperativity in Aminosilica Materials. *Appl. Catal. A Gen.* **2015**, *504*, 429–439.
5. Collier, V. E.; Ellebracht, N. C.; Lindy, G. I.; Moschetta, E. G.; Jones, C. W. Kinetic and Mechanistic Examination of Acid-Base Bifunctional Aminosilica Catalysts in Aldol and Nitroaldol Condensations. *ACS Catal.* **2016**, *6* (1), 460–468.
6. Weng, Z.; Yu, T.; Zaera, F. Synthesis of Solid Catalysts with Spatially Resolved Acidic and Basic Molecular Functionalities. *ACS Catal.* **2018**, *8* (4), 2870–2879.
7. Ge, T.; Hua, Z.; Zhu, Y.; Song, Y.; Tao, G.; Zhou, X.; Chen, L.; Ren, W.; Yao, H.; Shi, J. Amine-Modified Hierarchically Structured Zeolites as Acid-Base Bi-Functional Catalysts for One-Pot Deacetalization-Knoevenagel Cascade Reaction. *RSC Adv.* **2014**, *4* (110), 64871–64876.
8. Wang, D.; Wang, B.; Ding, Y.; Wu, H.; Wu, P. A Novel Acid-Base Bifunctional Catalyst (ZSM-5@$Mg_3Si_4O_9(OH)_4$) with Core/Shell Hierarchical Structure and Superior Activities in Tandem Reactions. *Chem. Commun.* **2016**, *52* (87), 12817–12820.
9. Zhang, X.; Liu, D.; Xu, D.; Asahina, S.; Cychosz, K. A.; Agrawal, K. V.; Al Wahedi, Y.; Bhan, A.; Al Hashimi, S.; Terasaki, O.; et al. Synthesis of Self-Pillared Zeolite Nanosheets by Repetitive Branching. *Science (80-.).* **2012**, *336* (6089), 1684–1687.
10. Liu, B.; Wattanaprayoon, C.; Oh, S. C.; Emdadi, L.; Liu, D. Synthesis of Organic Pillared MFI Zeolite as Bifunctional Acid-Base Catalyst. *Chem. Mater.* **2015**, *27* (5), 1479–1487.
11. Li, P.; Liu, H.; Yu, Y.; Cao, C.; Song, W. One-Pot Multistep Cascade Reactions over Multifunctional Nanocomposites with Pd Nanoparticles Supported on Amine-Modified Mesoporous Silica. *Chem. Asian J.* **2013**, *8*, 2459-2465.
12. International Zeolite Association. Database of Zeolite Structures. https://asia.iza-structure.org/IZA-SC/pow_plot_VerifSyn.php?STC=MFI&patternFN=Nano_Silicalite-1.dat